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INFRARED SPECTRUM OF UF_6 AT ELEVATED
TEMPERATURES

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ABSTRACT

The infrared spectrum of UF_6 was studied from 2-23 microns with a double beam spectrometer at temperatures up to 100°C . Six new bands were obtained. All of the available UF_6 bands were assigned and discussed. Values for the fundamental frequencies agreed very well with a recent study by Gaunt.³

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INFRARED SPECTRUM OF UF₆ AT ELEVATED TEMPERATURES

N. J. Hawkins, H. C. Mattraw, and D. R. Carpenter

INTRODUCTION

The infrared spectrum of UF₆ has been studied by several investigators. Bigeleison¹ studied the infrared spectrum from 2-17 μ with a single beam spectrometer. Later Burke, Smith, and Nielson,² extending the range from 2-40 μ with a double-beam spectrometer, studied the gas at room temperature (~ 125 mm vapor pressure) in cells of 10 cm and 1 meter length. Recently Gaunt³ studied UF₆ at room temperature from 2-25 μ in cells up to 180 cm path length with single-beam optics.

Since UF₆ sublimates to one atmosphere of pressure at 57°, ⁴ it seemed of interest to heat a pressurized cell containing UF₆ to find what new bands might be obtained and to increase the intensity of the "weak" bands.

EXPERIMENTAL

The infrared spectrograph employed was the Baird double-beam model AB2-195. NaCl and KBr optics were used to study the region from 2-23 μ . The cell was 10 cm in length and constructed of copper. The body of the cell was in the form of a 5-cm-OD screw. AgCl windows were set into the end caps and screwed to vacuum tightness against teflon gaskets. The UF₆ was condensed from an all-metal vacuum system into a side-arm trap attached directly to the infrared cell. Ribbon-type heaters were wrapped around the cell as well as around the attached gas-condensing assembly. To operate, the gas-condensing assembly was heated to drive the gas into the cell body at room temperature. The cell was then preheated to the temperature to be studied while the side arm was heated to a higher temperature. Immediately before the run the last remnants of solid or liquid UF₆ were removed from the windows by heating them for several minutes with an infrared lamp. It was noted in final blank background studies that there was no noticeable effect in the transmissive properties of the AgCl windows even after several UF₆ runs in which the inside cell temperature was close to 100°C where the vapor pressure of UF₆ was approximately 3000 mm.⁴

The UF₆ was obtained from two sources. Some was prepared at KAPL by the reactions between (1) U₃O₈ and CoF₃ and (2) UF₄ and AgF₂. In these preparations SiF₄ was an impurity which was difficult to remove completely. Later, UF₆ was obtained from the K-25 Laboratories at Oak Ridge. This material was found to contain HF, which was removed by a KF bed, and CO₂, which was removed by distillation at dry ice temperatures. All preparations, purifications, and material transfers were carried out under high vacuum conditions. None of the above impurities, in small amounts, interfere with the results reported. In fact, the SiF₄ band at 1032 cm⁻¹ was an excellent guide for determining which bands increased in intensity only as a result of pressure broadening.

The recorded spectra were calibrated with polystyrene in the NaCl region and 1, 2, 4 - trichlorobenzene in the KBr region.

RESULTS

The intensities observed on the Baird charts for a typical run in which the cell was heated beyond the point where there was definitely liquid UF_6 present are presented in Table I along with comparable intensities obtained at room temperature. Charts made from the recorded spectra are also included in this report. It is to be noted that bands considered "weak" at room temperature are "strong" at the higher temperature. All of the bands reported by Smith et al² in the 2-23 μ region are present. Gaunt³ found the bands at 755 cm^{-1} and 571 cm^{-1} which were not observed by Smith. However, we do not find Gaunt's band at 547 cm^{-1} , and while we suspect there is a band at 587 cm^{-1} we were not able to "develop" it sufficiently to be sure it was present because of the broadness of the ν_3 . In view of Gaunt's long path technique, the 587 cm^{-1} band is probably real. Completely new bands were observed at 1869, 1808, 1684, 1337, 533, and 479 cm^{-1} . The 533 cm^{-1} represents the peak of a rather broad band extending from 530-545 cm^{-1} , and may be due to more than one UF_6 ternary. In addition, there are indications of weak bands between 1400 and 1500 cm^{-1} which are easily explainable but do not warrant further consideration.

TABLE I

UF₆, g - OBSERVED INFRARED FREQUENCIES AT HIGH TEMPERATURES

ω_{obs}	% Absorption at Room Temp	% Absorption at High Temp	Assignment	ω_{calc}	Symmetry	Observer*
1869 cm^{-1}	-	3	$3\nu_3$	1869 cm^{-1}	$A_2+2F_1+F_2$	1
1808	-	3	$2\nu_3+\nu_2$	1782	$A_1+A_2+2E+F_1+F_2$	1
			or $\nu_1+\nu_2+\nu_3$	1824	F_1+F_2	
1684	-	8	$2\nu_2+\nu_3$	1695	$2F_1+F_2$	1
1337	-	9	$\nu_1+\nu_2+\nu_6$	1337	F_1+F_2	
			or $\nu_2+\nu_3+\nu_4$	1345	$A_1+A_2+2E+2F_1+2F_2$	1
1288	52	90-100	$\nu_1+\nu_3$		F_1	1,2,3
1159	59	90-100	$\nu_2+\nu_3$		F_1+F_2	1,2,3
852	12	59	$\nu_1+\nu_4$	851	F_1	1,2,3
825	33	90-100	$\nu_3+\nu_5$		$A_2+E+F_1+F_2$	1,2,3
755	-	14	$\nu_1-\nu_2+\nu_3$	752	F_1+F_2	1,3
715	16	67	$\nu_2+\nu_4$	722	F_1+F_2	1,2,3
672	73	90-100	$\nu_2+\nu_6$		F_1+F_2	1,2,3
623	90-100	90-100	ν_3		F_1	1,2,3
571	-	shoulder ν_3	$3\nu_4$	558	$A_1+2F_1+F_2$	1,3
533	-	677 broad	$\nu_4+\nu_5+\nu_6$	524	$A_1+A_2+2E+4F_1+3F_2$	1
			or $2\nu_5+\nu_6$	540	$A_1+E+2F_1+3F_2$	
479	-	14	$\nu_1-\nu_4$	479	F_1	1
			or $\nu_2-\nu_5+\nu_6$	470	$A_1+A_2+2E+2F_1+2F_2$	
392	-		$\nu_4+\nu_5$	388	$A_2+E+F_1+F_2$	2
			or $\nu_2-\nu_6$	400	F_1+F_2	
350	-		$\nu_2-\nu_4$ **	350	F_1+F_2	2
			or $\nu_5+\nu_6$	336	$A_1+E+F_1+F_2$	
279	-		$2\nu_5-\nu_6$	268	$A_1+E+2F_1+3F_2$	2
			or $-\nu_2+\nu_3+\nu_4$	273	$A_1+A_2+2E+2F_1+2F_2$	
			or $\nu_2+\nu_3+\nu_5$	289	$A_1+A_2+2E+2F_1+2F_2$	

*Observer

1 KAPL - this study

2 Burke et al

3 Gaunt

** Preferred value

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. <i>Hot UF₆ Study</i>				
DATE		INDEX		
13 JAN 54				
SAMPLE				
— <i>UF₆ Vapor ~100°C</i>				
--- <i>UF₆ Vapor ~25°C</i>				
<i>10 cm length cell</i>				
<i>AgCl window</i>				
FROM				
SAMP. CELL:	MM	CMS.		
REF. CELL	MM	CMS.		
CHEM.	MG.	MG.		
SOLV.	<i>Transmitted by DRC</i>			
VOL.	C.C.	%	C.C.	%
F.S. SOLID	°C	GAS	MM	

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-1

No. <i>Hot UF₆ Study</i>				
DATE		INDEX		
14 JAN 54				
SAMPLE				
— <i>UF₆ Vapor ~100°C</i>				
--- <i>UF₆ Vapor ~25°C</i>				
<i>10 cm cell length</i>				
<i>AgCl window</i>				
From				
Samp. Cell #	mm.	cm.		
Comp. Cell #	mm.	cm.		
Chem.	mg.	mg.		
Solv.	<i>Transmitted by DRC</i>			
Vol.	c.c.	%	c.c.	%
F.S. Solid	°C	GAS	mm.	

BAIRD ASSOCIATES
I. R. SPECTROPHOTOMETER
KBr Prism

Fig. 1132438--Hot UF₆ study.

DETERMINATION OF THE FUNDAMENTAL FREQUENCIES

Molecules of type YX_6 which belong to the O_h point group possess six fundamental vibration frequencies; namely, one nondegenerate A_g , one doubly degenerate E_g , and four frequencies which are triply degenerate of species F_{1u} , F_{2u} , F_{2g} (Table II). The symmetry of the dipole moment can only be F_{1u} .⁵ Thus only the bands containing the F_{1u} component, that is, only the ν_3 and ν_4 fundamentals, are active in the infrared. The ν_4 , while infrared active, is beyond the limit of observation of most optical systems. However, there are several observable binary and ternary combination bands from which values of the other fundamentals can be obtained.

Vibrations of type A_{1g} , E_g , and F_{2g} ⁵ are active in the Raman spectrum which has been observed by Bigeleisen et al.¹ The Raman data, that is, the ν_1 , ν_2 , and ν_5 , were obtained from liquid UF_6 and a solution of UF_6 in C_7F_{16} . To account for the combination bands in the infrared spectrum of the molecule in the gaseous state, it is necessary to assume that there are no perturbing effects caused by intermolecular interactions on the normal vibrations. Thus, we consider the Raman frequencies as an aid in assigning the binary combination bands, but take our "adjusted" fundamentals as those obtained from the binary combination bands.

TABLE II

FUNDAMENTAL VIBRATION FREQUENCIES OF UF_6 , g

Fundamental	Smith et al	Gaunt	KAPL	Symmetry
ν_1	656 cm^{-1}	668 cm^{-1}	665 cm^{-1}	A_{1g}
ν_2	511	532	536	E_g
ν_3	640	626	623	F_{1u}
ν_4	200	189	186	F_{1u}
ν_5	200	202	202	F_{2g}
ν_6	130	144	136	F_{2u}

The fundamental ν_3 was taken to be the observed value of 623 cm^{-1} . We have additional confidence in the value of ν_3 because of the band found at 1869 cm^{-1} which we assign as $3\nu_3$. The values for ν_1 , ν_2 , and ν_5 are obtained immediately from their binary bands in combination with ν_3 . The ν_6 was calculated from the combination band $\nu_2 + \nu_6$. The value of ν_4 was taken to be 186 cm^{-1} , the average of six bands which were thought to be combinations involving ν_4 . These data are summarized in Table III. It is to be noted that the peak of the band observed at 571 cm^{-1} is probably distorted by ν_3 . The true value is probably somewhat lower than the value observed.

TABLE III
COMBINATIONS INVOLVING ν_4

<u>ω_{obs}</u>	<u>Assignment</u>	<u>$\nu_4 \text{ calc}$</u>
852 cm^{-1}	$\nu_1 + \nu_4$	187 cm^{-1}
715	$\nu_2 + \nu_4$	179
479	$\nu_1 - \nu_4$	186
392	$\nu_4 + \nu_5$	190
350	$\nu_2 - \nu_4$	186
571	$3\nu_4$	190

It is to be noted in Table II that the KAPL values for the fundamentals are in good agreement with those obtained by Gaunt.³

THERMODYNAMIC PROPERTIES

Gaunt has calculated the thermodynamic properties of UF_6 from his spectral data. The value of the U-F distance was taken to be 2.00 Å. There would be only minor changes in the vibrational partition function which would be obtained from our values of the fundamentals. It is to be hoped that someday better data for the internuclear distances in spherical tops can be obtained because even small changes in this value would introduce large errors in the rotational partition function.

ASSIGNMENT OF THE OTHER NEW BANDS

In Table I the assignment of all the observed bands of UF_6 are summarized. For the band at 1808 cm^{-1} , $\nu_1 + \nu_2 + \nu_3$ is preferred because $\nu_1 - \nu_2 + \nu_3$ is the only possible assignment of the 755 cm^{-1} band consistent with our fundamentals. For the 350 cm^{-1} band observed by Smith and coworkers² we prefer $\nu_2 - \nu_4$ because $\nu_5 + \nu_6$ is not observed in MoF_6 and WF_6 . It might be possible, however, that $\nu_2 - \nu_4$ is present in the shoulders of stronger lines in Smith's traces of the MoF_6 and WF_6 spectra.

FURTHER STUDY

When CaF_2 windows become available, an attempt will be made to study further the important band at 1869 cm^{-1} , assigned as $3\nu_3$. It seems probable that the presence of this band leads to the preference for a set of fundamentals more in agreement with Gaunt than with Smith.

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